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Magnetism and Structure on Atomic Scale

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An efficient scheme is developed to study magnetism and structure on atomic scale. Starting by *ab initio* calculations of the elctronic structure in the framework of density functional theory, interaction potentials for molecular dynamics simulations of metallic nanostructures supported on metallic surfaces are carefully optimized.

The two methods are shortly explained. Examples for the application of the methods are given. Mainly electronic and structural properties of Co nanostructures on the Cu(001) surface are investigated.

1 Introduction

The essence of nanosience and technology is the ability to understand and manipulate matter at the molecular level. Structures behave differently when their dimensions are reduced to dimensions between 1 and 100 nm. Such structures show novel physical and chemical properties, due entirely to their nanoscopic size.

In the frontier field of nanomagnetism, understanding of the relationship of between magnetism and structure plays a central role. During the past few years experimental investigations of metallic nanostructures in the initial stage of heteroepitaxial growth revealed a lot of information which asks for a consistent theoretical explanation. Some important effects experimentally observed recently are:

- Surface alloying is found also for metals immiscible in bulk form (Co/Cu(001)).[1,2]
- Burrowing of Co clusters into Au, Cu and Ag surfaces has been observed.[3,4]
- It was observed, that the motion of adatoms on top of islands is is not the same as on a flat surface.[5]

During the last years we developed a combination of methods which can be used to study such effects in detail theoretically. First we will discuss the methods used for our calculations. Especially the newly developed method of quasi-*ab initio* molecular dynamics (QMD) simulations is discussed more in detail. Then we will discuss how the Korringa-Kohn-Rostocker (KKR) Green's function (GF) method is used to study magnetic properties of magnetic nanostructures on noble metal substrates. The QMD method is used to develop a new point of view on mismatch in heteroepitaxial growth. We distinguish between macroscopic and mesoscopic mismatch. This definition allows for a more detailed discussion and understanding of the dependence of surface and island related properties

on the size of the supported islands. Several of the above mentioned experimental results can be explained by using the *ab initio* techniques and MD simulations together. This is discussed for the adatom motion on supported islands and surface alloying.

2 Theoretical Methods

2.1 Calculation of Electronic Structure

The electronic structure calculations are carried out with the KKR Green's function method for surface defects.[6,7] The method is based on density functional theory in the local-spin-density approximation (LSDA).

By removing the atomic potentials of seven monolayers from a bulk crystal we create two half-crystals which are practically decoupled. In this way the surface can be treated as a localized two-dimensional perturbation of the bulk. Multiple scattering theory is applied to obtain the Green's function from the Dyson equation. The Green's function of the ideal surface is used as the reference Green's function for the calculation of the electronic properties of metallic nanostructures on the surface. The potential in a sufficiently large cluster around the supported nanostructure has to be considered as perturbed.

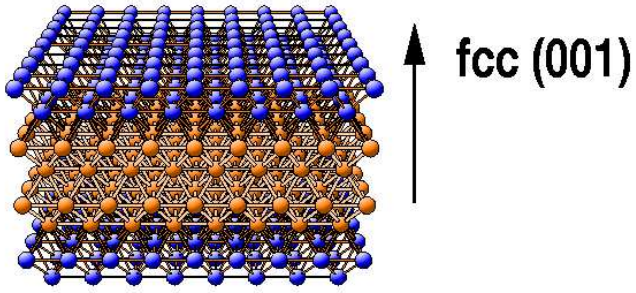

Figure 1. Structure to calculate the surface Green's function for the (001) surface of the fcc-structure (blue - decoupled half-crystals, brown - vacuum layers)

The full charge density is taken into account using a multipole expansion up to angular momentum $l_{max} = 6$. Coulomb and exchange correlation energies are evaluated using $l_{max} = 12$. For the latter ones the local functional of Vosko *et al.*[8] is used. Potentials are assumed to be spherically symmetric inside the Wigner-Seitz sphere.

2.2 Quasi - Ab Initio Molecular Dynamics

In the last few years we developed a method which connects the *ab initio* electronic structure calculations with large scale molecular dynamic simulations. Our approach is based on fitting of the interaction parameters of potentials for molecular dynamic simulations to accurate first-principle calculations of selected cluster-substrate properties and bulk properties of the system under investigation.

To describe metallic clusters on noble metal substrates many body potentials in the second moment tight-binding approximation are used.[9]

The cohesive energy E_{coh} is the sum of the band energy E_B and the repulsive part E_R:

$$E_{coh} = \sum_i \left(E_R^i + E_B^i\right) \tag{1}$$

$$E_B^i = -\left(\sum_j \xi_{\alpha\beta}^2 \exp(-2q_{\alpha\beta}(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1))\right)^{1/2} \tag{2}$$

$$E_R^i = \sum_j \left(A_{\alpha\beta}^1(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1) + A_{\alpha\beta}^0\right) \exp(-p_{\alpha\beta}(\frac{r_{ij}}{r_0^{\alpha\beta}} - 1)) \tag{3}$$

where r_{ij} represents the distance between atoms i and j, and $r_0^{\alpha\beta}$ is the first-neighbor distance in the $\alpha\beta$ lattice structure, while it is just an adjustable parameter in the case of the cross interaction. ξ is an effective hopping integral that depends on the material, and $q_{\alpha\beta}$ and $p_{\alpha\beta}$ describe the dependence of the interaction strength on the relative interatomic distance.

We will explain the method for the system Co/Cu(001). Co and Cu are not miscible in bulk form. Therefore the determination of the cross interaction is a problem. We solve the problem by a careful fitting to accurate first-principles calculations of selected cluster-substrate properties. The result is a manageable and inexpensive scheme able to account for structural relaxation and including implicitly magnetic effects, crucial for a realistic determination of interatomic interactions in systems having a magnetic nature. After determination of the Cu-Cu parameters which are fitted to experimental data only[9] the Co-Co and Co-Cu parameters are optimized simultaneously by including in the fit the results of first-principles KKR calculations. To this purpose, we have taken the solution energy of single Co impurity in bulk Cu[10] $E_S^{Co\ in\ Cu}$, energies of interaction of two Co impurities in Cu bulk[11] $E_{1,b}^{Co-Co}$, $E_{2,b}^{Co-Co}$ and binding energies of small supported Co clusters on Cu(001) $E_{1,on\ Cu(100)}^{Co-Co}$, $E_{1,in\ Cu(100)}^{Co-Co}$ (terrace position), $E_{on\ Cu(100)}^{trimer}$, $E_{on\ Cu(100)}^{2x2\ island}$.

The set of data used to define the potential and the corresponding values calculated by means of the optimized potential are given in Table I. The bulk and surface properties are well reproduced.

The quality of the potential was tested in different ways. The *ab initio* datapool contains only ideal lattice structures, i.e. relaxations are not taken into account. Recently, the KKR Green's function method was extended to take into account the effect of lattice relaxations.[12] Calculations of the lattice distortion in the vicinity of a Co impurity in Cu bulk have been performed with the KKR-GF method. Our QMD method shows a good agreement with this results. The second test of our potential is done performing calculations of interlayer distances in Co/Cu multilayers. A detailed LEED study of the Co/Cu(100) films for different Co coverages was performed in Kirschner's group.[13] Interlayer spacing was determined for different Co coverages. We use our potentials to determine interlayer distances performing energy minimization calculations. The results demonstrate that the agreement with experiment is rather good. Therefore we believe that the parametrisation developed in our paper gives a good description of the Co-Cu bonds. Applications of the potential are given later in the article.

	Quantity	Data	fitted value
Cu	a_{Cu}	3.615 Å	3.614 Å
(fcc)	E_c	3.544 eV	3.545 eV
	B	1.42 Mbar	1.42 Mbar
	C_{11}	1.76 Mbar	1.76 Mbar
	C_{12}	1.25 Mbar	1.25 Mbar
	C_{44}	0.82 Mbar	0.82 Mbar
Co	a_{Co}	2.507 Å	2.515 Å
(hcp)	E_c (E)	4.386 eV	4.395 eV
	B	1.948 Mbar	1.989 Mbar
	C_{11}	3.195 Mbar	3.337 Mbar
	C_{12}	1.661 Mbar	1.426 Mbar
	C_{13}	1.021 Mbar	1.178 Mbar
	C_{33}	3.736 Mbar	3.665 Mbar
	C_{44}	0.824 Mbar	0.646 Mbar
Co-Cu	$E_S^{Co\ in\ Cu}$	0.4 eV	0.38 eV
	$E_{1,b}^{Co-Co}$	-0.12 eV	-0.18 eV
	$E_{2,b}^{Co-Co}$	0.03 eV	-0.05 eV
	$E_{1,on\ Cu(100)}^{Co-Co}$	-1.04 eV	-1.04 eV
	$E_{1,in\ Cu(100)}^{Co-Co}$	-0.26 eV	-0.35 eV
	$E_{on\ Cu(100)}^{trimer}$	-2.06 eV	-1.96 eV
	$E_{on\ Cu(100)}^{2x2\ island}$	-3.84 eV	-3.86 eV

Table 1. Data used for the fitting of the potential together with the values calculated with the optimized potential. (Cohesive energy E_c, bulk modulus B, elastic constants C_{ij} from Cleri *et al.*[9], first and second neighbor interaction energies $E_{1,b}^{Co-Co}$, $E_{2,b}^{Co-Co}$ from Drittler *et al.*[10] , solution energy $E_S^{Co\ in\ Cu}$ from Hoshino *et al.*[11], binding energies of small Co clusters $E_{1,on\ Cu(100)}^{Co-Co}$, $E_{1,in\ Cu(100)}^{Co-Co}$, $E_{on\ Cu(100)}^{trimer}$, $E_{on\ Cu(100)}^{2x2\ island}$ are calculated using KKR Green's function method.)

3 Magnetic Properties of Nanostructures on Metallic Surfaces

Using the KKR Green's function method we have studied the properties of $3d$, $4d$ and $5d$ adatoms on Ag(001),Pd(001) and Pt(001) systematically.[14,15] One central point of investigation was the study of imperfect nanostructures. We have investigated the influence of Ag impurities on the magnetism on small Rh and Ru clusters on the Ag(001) surface.[16] The change of the magnetic moments could be explained in the framework of a tight-binding model. Nevertheless it was observed that the magnetism of Rh nanostructures shows some unusual effects.[17] An anomalous increase in the magnetic moments of Rh adatoms on the Ag(001) surface with decreasing interatomic distance between atoms was observed, whereas for dimers of other transition metals the opposite behavior is observed.

3.1 Mixed Co-Cu Clusters on Cu(001)

The magnetic properties of Co nanostructures on Cu substrate can be strongly influenced by Cu atoms. For example, Cu coverages as small as three hundredths of a monolayer

drastically affect the magnetization of Co films.[18] Experiments and theoretical studies demonstrated that magnetization of mixed clusters of Co and Cu depends on the relative concentration of Co and Cu in a nonobvious way. Quenching of ferromagnetism in Co clusters embedded in copper was reported.[19] Calculations by means of the QMD method showed that surface alloying is energetically favorable for in the case of Co/Cu(001) and mixed Co-Cu clusters are formed in the early stages of heteroepitaxy. Recent experiments[2] suggest that mixed Co-Cu clusters indeed exist.

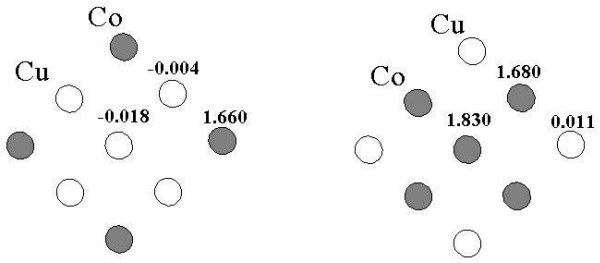

Figure 2. Spin polarization of Co-Cu mixed clusters on Cu(001). Magnetic moments in Bohr magnetons are given for all inequivalent site.

We have studied all possible mixed configurations in 3×3-atoms islands on Cu(001) surfaces. We observe a small induced moment at the Cu atoms in the island and a decrease of the moments at the Co atoms in comparison with the 3×3 Co-island. A stronger reduction of the Co moments is achieved, if the Co_9 cluster is surrounded by a Cu brim and capped by a Cu cluster. A reduction of 14 % is obtained for the average moment of the Co_9 cluster. This effect should have a strong influence on the properties of the Co-Cu interface in the early stages of growth. Coating of Co clusters with Cu atoms has been found recently in experiments.[4]

4 Strain and Stress on the Mesoscale

4.1 The Concept of Mesoscopic Misfit

If some material is grown on a substrate with a different bond length the lattice mismatch is at the interface leads to strain fields. Strain can be relieved through the introduction of defects in the atomic structure, such as dislocations, or by an atomic rearrangement. Usually strain relaxations are predicted on the basis of the macroscopic lattice mismatch between the two materials. However, if the deposited system is of mesoscopic size of several 100 atoms, its intrinsic bond lengths are different from the bond length in the bulk materials. For the Co/Cu(001) interface the *macroscopic* mismatch m_0 between Co and Cu defined as $m_0 = (a_{Cu} - a_{Co})/a_{Cu}$ (a_{Cu} and a_{Co} are the lattice constants) is only $\approx 2\%$. Several recent experiments have suggested that strain relaxations for submonolayer

coverage[20] or even for a few monolayers[21] cannot be explained by the macroscopic misfit between bulk materials.

In order to get a deeper insight into the local strain relaxations on an atomic scale, the equilibrium geometries of plane square Co islands of different sizes (up to 600 atoms) on Cu(001) are calculated by computing the forces at each atomic site and relaxing the geometry of islands and the substrate atoms by means of the quasi-*ab initio* method.

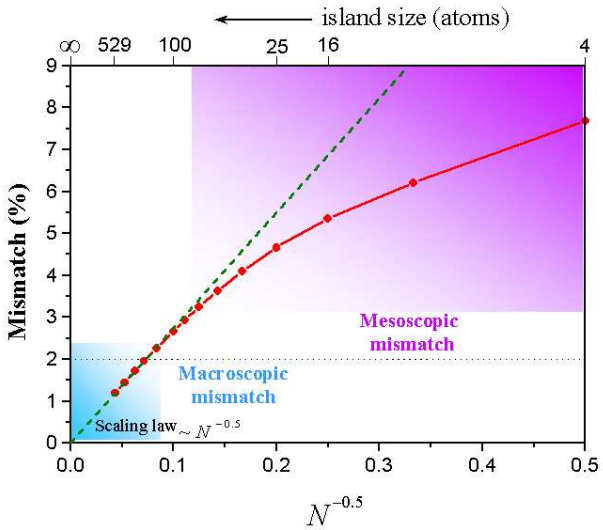

Figure 3. Size-dependent mismatch $m = (r_b^{Cu} - r^{Co})/r_b^{Cu}$ for the Co square islands on Cu(001) (r_b^{Cu} - first bond length for Cu bulk; r^{Co} - average bond length in Co islands

In Fig. 2.1 we show the change in the mismatch with the size of Co islands. It is seen, that the mesoscopic mismatch between small Co islands and the substrate is considerably larger than the mismatch calculated from the lattice constants of the two materials. Only for Co islands incorporating more than 200 atoms the local strain can be described by the macroscopic mismatch. We found that both the mesoscopic and macroscopic mismatch depend on the size of the islands and for islands larger than 60 atoms mismatch scales like $N^{-0.5}$ (N - number of atoms in islands). Such scaling behavior is determined by the relaxations of the edge atoms of the islands whose number changes as $\sqrt{N}$. One very fundamental issue predicted by these results is the possible strong impact of the size dependent mismatch on the local strain field. The substrate can dynamically respond to the growth of islands and can exhibit a strong inhomogeneous strain distribution during the growth process.

4.2 Strain and Adatom Motion on Mesoscopic Islands

The mesoscopic mismatch or mesoscopic strain depend strongly on the size of the clusters. Therefore we expect that also the barriers for hopping diffusion depend on the size of the

clusters. The calculations show, that the barriers for hopping on the small Co islands (16-50 atoms) are found to be about $\approx 20\%$ lower than those on the large islands (100-500 atoms) (cf. Fig. 3.1). The diffusivity D is related to the hopping rate of single adatoms by $D = D_0 \cdot exp(-E_d/kT)$, where E_d is the energy barrier for hopping, D_0 is the prefactor. We found that D_0 is nearly the same for all islands, therefore the diffusion coefficient D on small Co islands at room temperature is found to be about two orders of magnitude larger than that on large Co islands.

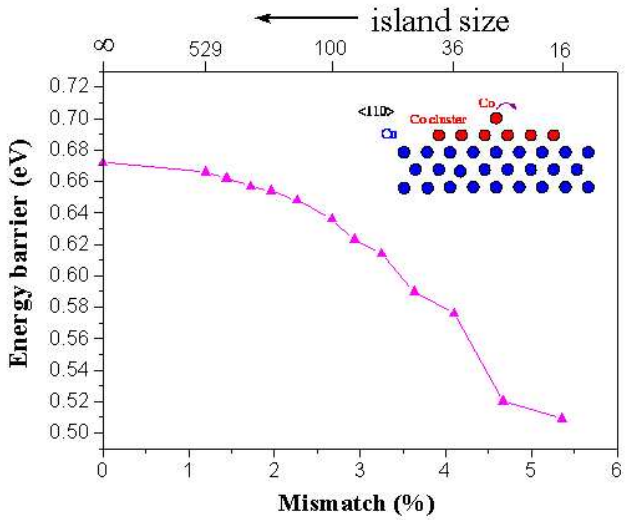

Figure 4. Strain dependence of energy barrier for hopping diffusion on top of Co square islands. Since the strain depends on island size, the activation barrier for diffusion depends also on island size (see upper horizontal scale).

5 Surface Alloying

In the past few years, much research has been performed on surface alloys. The most remarkable finding is that place exchange processes can result in the formation of surface alloys, even for metals immiscible in bulk form. For example it was concluded that Co atoms intermix with Cu at the Cu(100) surface by an atomic exchange process.[1] Also burrowing of Co clusters into Au, Cu and Ag substrates has been observed.[3]

When a material A is deposited on a surface B one needs to know whether intermixing takes place and whether A atoms are isolated or form clusters in a surface layer. Simple arguments to understand the atomic behavior on surfaces are based on such macroscopic properties as surface and interface energies of the components. However they are rather questionable when applied to individual adatoms on a metal surface, whose interaction determines the atomic picture in the early stages of thin-film growth.

The KKR Green's function method was used to study the energetics of surface alloying of 3d adatoms on an atomic scale.[22] Differences in total energy between the initial (A) and

the final (B) configuration of the atomic exchange process are calculated.

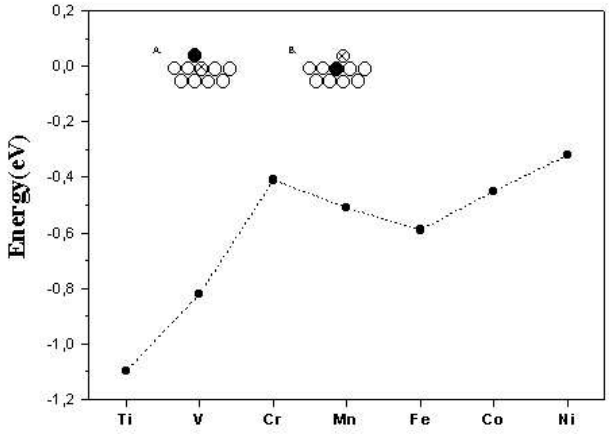

Figure 5. Energetics of the exchange process. Energy difference between complex B and A is presented.

Surprisingly, we find that for all $3d$ impurities it is energetically favorable to exchange with Au surface atoms. The energy gains are large for all impurities. For Fe, Co, and Ni impurities our calculations support the conclusions of the experimental investigations.[23,24] The results suggest, that a simple model of epitaxial growth based on an abrupt boundary between components can be inadequate to describe structural and magnetic properties of 3d nanostructures on a gold surface. All $3d$ adatoms considered in the investigation are magnetic on the Au(100) surface. Calculations of paramagnetic Co adatoms on Au(100) show, that magnetism tends to stabilize Co on the surface and prevents site exchange.

It was shown by Hoshino *et al.*[11] that the fundamental characteristic features of the phase diagrams can be qualitatively explained by the nearest-neighbor interaction of impurity pairs. The attractive interaction leads to segregation, the repulsive one to a solid solution. Thus, the calculation of the interaction energy of impurity pairs at the surface should provide information about cluster formation processes at the surface. The interaction energies of 3d impurities at nearest-neighbor sites on the surface (adatom positions) and in the first surface layer (terrace position) of Au(100) have been calculated. Negative energy means attraction and positive energy repulsion between adatoms. Only Fe and Co impurities show an attraction which is weak and not significantly different from zero.

Acknowledgments

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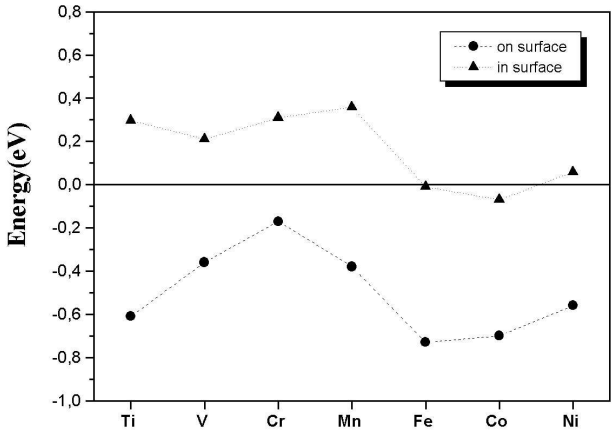

Figure 6. Interaction energies of $3d$ impurities on the nearest neighbor sites on the Au(100) surface and in the surface layer

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